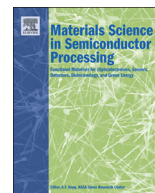




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## Structural, optical dispersion and dielectric properties of novel chromium nickel organic crystalline semiconductors

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## ABSTRACT

A novel organic crystalline semiconductor, [Cr(DPPP)(DPPM)(Ni-ap)(CO)<sub>2</sub>] (Cr–Ni OSC) (6a), (DPPP=diphenylphosphino-propanone, DPPM=diphenylphosphino-methane and Ni-ap=nickel apyrazole ring) (6a) was synthesized. Structural characteristics of the Cr–Ni OSC complex have been investigated by IR, <sup>1</sup>HNMR, <sup>31</sup>P NMR, thermal analysis (TG/DTA), and XRD. Thermal analysis of Cr–Ni OSC implies that, the complex was thermally stable up to 218 °C, and the melting point of it was 193 °C. Two discrete regions of (44.46%, 128–421 °C) and (41.15%, 600–823 °C) by TG analysis of Cr–Ni OSC complex was determined. XRD crystal data of Cr–Ni OSC showed the formation of monoclinic (P2<sub>1</sub>/n). Transmittance and reflectance have been used to determine the optical dispersion and dielectric properties of the Cr–Ni OSC complex in the range of 200–800 nm. The transparency of the complex is 75–80% in the visible range. The optical and transport energy gaps were estimated as 1.87 eV and 2.01 eV respectively. Optical dispersion parameters have been calculated by using single term Sellmeier dispersion relation and Wemple–DiDomenico single oscillator model. Several dispersion parameters were determined by analysis of refractive index dispersion. The optical conductivity, surface and volume energy loss functions, and the electric modulus were also estimated from the optical dielectric constant analysis.

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## 1. Introduction

The field of organic electronics is rapidly maturing into one where new applications and products are currently in development. It is an active emerging technology with immense promise for innovative, convenient and high performance electronics. Organic devices offer an attractive balance between cost and performance, complemented by versatility and functionality accomplished by means of molecular engineering [1–5].

The physical properties of diphenyl phosphino organic semiconductors have drawn great attention from scientists and engineer's point of view, because of their extensive use of technological devices such as organic light emitting diodes (OLEDs) [6,7], and organic–inorganic heterojunctions [8]. A pyrazole derivatives ring (PyDR) of 1,3 bis (diphenyl phosphino) propanone chromium tetracarbonyl DPPP and DPPM is one of the best important organic compounds owing to its high electrical conductivity and mobility for optoelectronic applications [9].

DPPP and DPPM are key targets in the chemistry of organophosphorus compounds. They are widely used as ligands for metal complex, which contain N–H functional groups and their ability to participate intimately within the

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formation of semiconductors of transition metal complexes. Such cooperation between diphenylphosphino methane ligand (DPPM) and the transition metal center has certainly led to substantial improvements in many organic semiconductors [6–10]. The role of N–H functional groups in organic semiconductors and catalysis has recently been examined in great detail by Ding [9]. One significant area of interest has been the development of diphenyl phosphinomethane ligands containing N–H functionalities. Perhaps one of the most important and early contributions to this field is the work in which the synthesis, elucidation of charge transport and optical parameters in the 1CR-dppm organic crystalline semiconductors are given [11]. The phosphines are very popular ligands in transition metal ion complexes [12–17]. Their steric and electronic effects have a remarkable effect on organic transformations that take place by the transition metal centers [18].

For the design of optoelectronic devices, precise information of the optical dispersion and dielectric parameters is a significant factor. Although different experimental studies have been declared in the optical and dielectric properties of p-conjugated organic compounds [19–26], there are few reports on the dispersion parameters, optical constants, dielectric parameters, optical conductivity, electric modulus, dielectric relaxation time, the surface energy loss function, volume energy loss function parameter of related compounds of PyDR of DPPP and DPPM semiconductor in the available literature [27–30]. Suitable optical properties of the organic semiconductors, such as reflectivity, refraction, and absorption are significant factors for the analysis and design of the optical recording medium. On the other hand, organic semiconductor of PyDR derivatives plays a significant role in fabricating many new optoelectronic and electronic devices. So, we have strived to cover more optical properties of PyDR of DPPP and DPPM organic semiconductor.

In this work, our aim is to synthesize high quality Cr–Ni OSC organic crystalline semiconductors complexes. Also, the structural characteristics of the Cr–Ni OSC by different techniques are determined. Furthermore, optical parameters are obtained and interpreted based on single term Sellmeier dispersion relations and Wemple–DiDomenico single oscillator model. Moreover, the optical band gap, the transport gap and the binding energy of Cr–Ni OSC complex are obtained based on the feasibility of the band theory for the main absorption edge analysis. Eventually, a comparative study between Cr–Ni OSC complex and other p-conjugated organic compounds formerly deposited by different methods are reported.

## 2. Experimental details

### 2.1. Synthesis, solubility study and growth of single crystals

The commercially available chemicals that were used without further purification are:  $\text{NiCl}_2(\text{II}) \cdot 6(\text{H}_2\text{O})$ ,  $\text{Cr}(\text{CO})_6$  99.9%. Dichloromethane was dried by refluxing over calcium hydride under dinitrogen, distilled under nitrogen and stored in a closed ampoule over 4 Å molecular sieves and frozen/pumped/thawed three times to remove all dissolved gases.

A mixture of 1:1 mol ratio of DPPPC (1a) (5.94 g, 0.01 mol) and bis(diphenylphosphino)methane (DPPM) (1a') (3.48 g,

0.01 mol) was refluxed in n-decane, at 80 °C, 4 h under nitrogen. The obtained pale yellow product (2a) was washed with acetone and recrystallized to increase the purity. IR spectra (KBr pellet,  $\text{cm}^{-1}$ ): 3025w, 2053s, 1998s, 1982m, 1971w, 1801m, 1797m, 1584w, 1475ws, 726s, 689s.  $^1\text{H NMR}$   $\delta_{\text{H}}$  (500 MHz;  $\text{DMSO-d}_6$ ): 1.27 (2H, s,  $-\text{P}-\text{CH}_2-\text{P}-$ ), 2.01 (2H, s,  $-\text{P}-\text{CH}_2-\text{CH}_2-$ ), 2.73 (2H, s,  $-\text{P}-\text{CO}-\text{CH}_2-$ ), 7.28–7.90(40H, s, aromatic ring).

One mole of product (9.20 g, 0.01 mol) (2a) and two moles of acetone (1.16 g, 0.01 mol) were refluxed in n-decane (condensation reaction), at 80 °C, 3 h under nitrogen. The obtained brown product (3a) was washed with acetone and recrystallized to increase the purity. IR spectra (KBr pellet,  $\text{cm}^{-1}$ ): 3030 w, 2042s, 2010s, 1979m, 1807m, 1799m, 1587sh, 1480w, 720s, 690s.  $^1\text{H NMR}$   $\delta_{\text{H}}$  (500 MHz;  $\text{DMSO-d}_6$ ): 1.63 (6H, s,  $\text{C}(\text{CH}_3)_2-\text{C}=\text{C}-\text{P}-$ ), 1.80 (3H, s,  $-\text{C}(\text{CH}_3)-\text{C}=\text{C}-\text{CH}_2-$ ), 2.11 (2H, s,  $-\text{P}-\text{CH}_2-\text{C}=\text{C}-$ ), 2.83 (3H, s,  $-\text{C}(\text{CH}_3)-\text{C}=\text{C}-\text{CO}-$ ), 7.15–7.83(40H, s, aromatic ring).

Application of Micheal addition reaction for this step by a mixture of 1:2 mol ratio of (3a) (9.98 g, 0.01 mol) and hydrazine hydrate (0.64 g, 0.01 mol) was refluxed in n-decane, at 80 °C, 1 h under nitrogen. A pale brown product (4a) was washed with diethyl ether and recrystallized to increase the purity. IR spectra (KBr pellet,  $\text{cm}^{-1}$ ): 3270mb, 3134ws, 3035m, 2047s, 2008s, 1983m, 1823m, 1797s, 1590sh, 1482m, 796s, 737s, 719s.  $^1\text{H NMR}$   $\delta_{\text{H}}$  (500 MHz;  $\text{DMSO-d}_6$ ): 1.29 (6H, s,  $\text{H}_2\text{N}-\text{NH}-\text{C}(\text{CH}_3)_2-$ ), 1.38 (6H, s,  $\text{H}_2\text{N}-\text{NH}-\text{C}(\text{CH}_3)_2-$ ), 1.51(2H, s,  $-\text{P}-\text{CH}_2-\text{CH}-$ ), 2.17 (6H, b,2  $-\text{C}(\text{CH}_3)-\text{NH}-\text{NH}_2$ ), 6.23 (1H, sm,  $-\text{P}-\text{CO}-\text{CH}-$ ), 6.61(1H, sm,  $-\text{P}-\text{CH}-\text{P}-$ ), 7.32–7.69(40H, s, aromatic ring).

Elimination two moles of water from this compound (4a) (1.06 g, 0.001 mol) and addition two moles of acetyl acetone (0.2 g, 0.001 mol) by a mixture of 1:2 mol ratio was refluxed in toluene, at 80 °C, 6 h under nitrogen. A brown product (5a) was washed with diethyl ether and recrystallized to increase the purity. IR spectra (KBr pellet,  $\text{cm}^{-1}$ ): 3430s, 3336s, 3245b, 3041m, 2040s, 2010s, 1987m, 1808m, 1793m, 1573sh, 1486s, 754s, 717s, 786s.  $^1\text{H NMR}$   $\delta_{\text{H}}$  (500 MHz;  $\text{DMSO-d}_6$ , ppm): 1.26 (6H, s,  $-\text{N}-\text{NH}-\text{C}(\text{CH}_3)_2-$ ), 1.35(6H, s,  $-\text{N}-\text{NH}-\text{C}(\text{CH}_3)_2-$ ), 1.63(2H, s,  $-\text{P}-\text{CH}_2-\text{CH}-$ ), 2.16 (6H, m,  $\text{CH}_3-\text{C}-\text{CH}_2-$ ), 1.86 (6H, m,  $-\text{N}=\text{C}-\text{CH}_3$ ), 2.53 (2H, b,  $-\text{C}(\text{CH}_3)-\text{NH}-\text{N}-$ ), 2.93 (4H, m,  $\text{CH}_3-\text{CO}-\text{CH}_2-$ ), 6.05 (1H, sm,  $-\text{P}-\text{CO}-\text{CH}-$ ), 5.36(1H, sm,  $-\text{P}-\text{CH}-\text{P}-$ ), 7.32–7.69 (40H, s, aromatic ring).

Finally, reflux one mole of  $\text{NiCl}_2$  (0.128 g, 0.001 mol) with one mole of compound (5a) (0.123 g, 0.001 mol) was carried out in toluene, at 85 °C, 6 h. A pale yellow product (Cr–Ni OSC) (6a) was washed with diethyl ether and recrystallized to increase the purity. The reaction scheme is shown in Fig. 1. IR spectra (KBr pellet,  $\text{cm}^{-1}$ ): 3065w, 2042s, 1998m, 1982m, 1971w, 1813s, 1587sh, 1490m, 773w, 721s, 690s.  $^1\text{H NMR}$   $\delta_{\text{H}}$  (500 MHz;  $\text{DMSO-d}_6$ , ppm): 1.36 (6H, s,  $-\text{Ni}-\text{N}-\text{C}(\text{CH}_3)_2-$ ), 1.47(6H, s,  $-\text{N}-\text{N}-\text{C}(\text{CH}_3)_2-$ ), 1.75 (2H, s,  $-\text{P}-\text{CH}_2-\text{CH}-$ ), 1.96(3H, m,  $-\text{N}=\text{C}-\text{CH}_3$ ), 2.24 (3H, s,  $-\text{CH}-\text{CO}-\text{CH}_3$ ), 2.30(3H, m,  $-\text{N}=\text{C}-\text{CH}_3$ ), 2.46(3H, s,  $-\text{CH}-\text{C}-\text{CH}_3$ ), 3.65(1H, m,  $\text{CH}_3-\text{C}=\text{CH}-$ ), 5.37(1H, m,  $-\text{Ni}-\text{CH}-\text{CO}-$ ), 6.25(1H, m,  $-\text{P}-\text{CH}-\text{P}-$ ), 6.72 (1H, m,  $\text{P}-\text{CO}-\text{CH}-$ ), 7.32–7.69(40H, s, aromatic ring).

Choose a solvent ( $\text{CH}_2\text{Cl}_2$  solvent) in which Cr–Ni OSC complex is moderately soluble. If the solute is too soluble, this will result in small crystal size. Avoid solvents in

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